

US EPA ARCHIVE DOCUMENT



# POPs and other Anthropogenic SOCs in Eurasian Air Masses Measured at a Rural Site in Okinawa, Japan

## Overview

### Why Measure Airborne Pollutants in Eurasian Air Masses?

#### Background

Persistent organic pollutants (POPs) and other semi-volatile organic compounds (SOCs) may undergo long range atmospheric transport (figure from Eurasian emission sources and in the Pacific Northwest Coast region of the United States (Figure 2).

Besides the increased environmental risk to sensitive high elevation ecosystems, there also exists a potential for the air quality to be decreased in the Western U. S. during trans-Pacific transport events.

#### Objective

The objective of this research is to identify POPs and other anthropogenic SOCs in Eurasian air masses, and to use these compounds as tracers for Eurasian air emissions.

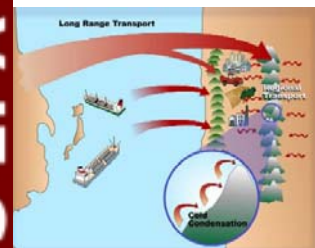


Figure 1: Schematic of the potential sources of anthropogenic SOCs to the eastern portion of the United States

### How to Measure POPs and SOCs

- Air masses are sampled and analyzed for POPs and other anthropogenic SOCs at sites close to Eurasian emission sources and in the Pacific Northwest Coast region of the United States (Figure 2).

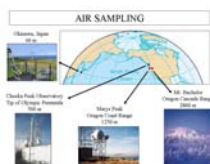


Figure 2: Air Sampling Stations operated by the Simonich Environmental Chemistry Laboratory

#### Sampling in Okinawa

- High volume air sampling (~644 m<sup>3</sup> in a 24 hour period) was conducted during a six week campaign from March 19 to May 1, 2004 (Figure 3).

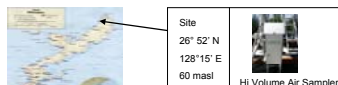


Figure 3: Hi Volume Air Sampler was located near Hedo Point in Okinawa, Japan

- The gas phase was collected using a combination of polyurethane foam and XAD-2 resin, while the particle phase was collected using quartz fiber filters.

- Eighty two POPs and SOCs were selected for this research project including emissions from combustion (polycyclic aromatic hydrocarbons (PAHs)), agricultural (pesticides), and industrial ( polychlorinated biphenyls (PCBs)) sources.

Table 1: Analytes

Electron Impact Ionization (EI)	Electron Capture Negative Ionization (ECNI)
<b>PAHs:</b> Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene <b>Pesticides and degradation products:</b> o,p'-DDT, p,p'-DDT, o,p'-DDD, o,p'-DDD, o,p'-DDE, p,p'-DDE, Dieldrin, Dieldrin S, Ethion, Etrazaprole, Malathion, Parathion and Methyl Parathion, Phorate, Metolachlor, Methoxychlor, Acetochlor, Alachlor, Prometon, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine <b>Surrogates:</b> d <sub>10</sub> -Fluorene, d <sub>10</sub> -Phenanthrene, d <sub>10</sub> -Pyrene, d <sub>12</sub> -Triphenylene, d <sub>12</sub> -Benzo[a]pyrene, d <sub>12</sub> -Benzo[ghi]perylene, d <sub>12</sub> -EPTC, d <sub>12</sub> -Phorate, d <sub>12</sub> -Atrazine, d <sub>12</sub> -Dieldrin, d <sub>12</sub> -Malathion, d <sub>12</sub> -Parathion, d <sub>12</sub> -p,p'-DDE, d <sub>12</sub> -p,p'-DDT, d <sub>12</sub> -Methyl Parathion, d <sub>12</sub> -Alachlor, d <sub>12</sub> -Acetochlor <b>Internal Standards:</b> d <sub>10</sub> -Acenaphthene, d <sub>10</sub> -Fluoranthene, d <sub>10</sub> -Benzo[k]fluoranthene	<b>PCBs:</b> PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3,4,4',5-Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB 183 (2,2',3,4,4',5'-6-Heptachlorobiphenyl), and PCB 187 (2,2',3,4,4',5,5'-6-Heptachlorobiphenyl) <b>Pesticides and degradation products:</b> Hexachlorocyclohexanes (HCH) - α, β, γ (lindane), and δ, Chlordane - cis, trans, oxy, Nonachlor - cis, trans, Heptachlor, Heptachlor Epoxide, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalnil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex <b>Surrogates:</b> <sup>13</sup> C <sub>12</sub> -PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), <sup>13</sup> C <sub>12</sub> -PCB 180 (2,2',3,4,4',5,5'-Heptachlorobiphenyl), d <sub>12</sub> -Chlorpyrifos, <sup>13</sup> C <sub>12</sub> -HCB, d <sub>12</sub> -γ-HCH, d <sub>12</sub> -Endosulfan I, d <sub>12</sub> -Endosulfan II <b>Internal Standards:</b> d <sub>12</sub> -Trifluralin

- The samples were extracted using accelerated solvent extraction and analyzed using GC/MS (Electron Impact and Electron Capture Negative Ionization).

## Preliminary Results

### Tracking Air Pollution and its Chemical Signature

- The preliminary results of two of the twenty collected samples are presented below.
- Ten day back trajectories were calculated every three hours, using NOAA's HYSPLIT, for a twenty four hour sample and uploaded into ArcMap (ESRI, Redland, CA).



Figure 4: Ten day back trajectories for every three hours over the twenty hour sampling period uploaded into ArcMap. The sample collected on March 23rd 2004 is in blue and the sample collected on April 2nd 2004 is in red.

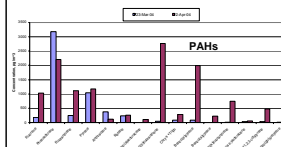


Figure 5: A comparison of the polycyclic aromatic hydrocarbons (PAHs) of the samples collected on the 23rd of March and 2nd of April 2004.

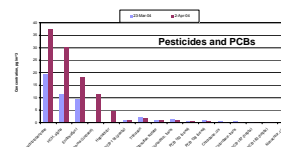


Figure 6: A comparison of the polychlorinated biphenyls (PCBs) and pesticides of the samples collected on the 23rd of March and 2nd of April 2004.

### Combustion Source Apportionment:

Table 3: Comparison of various PAH ratios with their corresponding sampling day (5).

Source	FI/(FI + Py)	IP/(IP+Bghi)	Ba/(BaA + Chrys + Triph)
23-Mar-04	0.19	0.74	0.04
2-Apr-04	0.49	0.60	0.27
Diesel	0.6 to 0.7	0.35 to 0.70	0.38 to 0.64
Gasoline	0.40	0.18	0.43
Wood	0.74	0.69	0.56
Coal	0.48 to 0.6	0.48 to 0.57	0.18 to 0.5

### Conclusions

- Long range atmospheric transport is occurring to the island of Okinawa.
- Various pesticides, PCBs, and PAHs were measured in Okinawa.
- Further analysis of more samples will help further identify the combustion sources through the use of PAH ratios and other chemical indicators.
- Detected higher concentrations of most pollutants in the sample collected on April 2nd 2004. This sample also corresponds to the trajectories arriving to Okinawa directly from Asia.

### Future Work

- Extract and analyze the remaining 20 samples/blanks from Okinawa.
- Continue sampling at Mt Bachelor
- Possible 1 year campaign in Okinawa

### Looking for more information:

<http://www.oregonstate.edu/~simonich/>  
(Simonich Environmental Chemistry Laboratory)

### Acknowledgments

- EPA: STAR Fellowship!
- National Institute of Environmental Studies
- Tokyo Metropolitan University
- Dr. Staci Simonich's Research Group (Oregon State University)
- Dr. Dan Jaffe's Research Group (University of Washington)
- Frontier Geosciences (Seattle, WA)
- National Science Foundation Career

### References:

- (1)Wania, F. a. M., D. *Environmental Science & Technology* **1996**, 30, 390A-396A.
- (2)Simonich, S. L.; Hites, R. A. *Science* **1995**, 269, 1851-1854.
- (3)Kirkmick, J. O. et al. *Environmental Science & Technology* **2001**, 35, 2690-2697.
- (4)Blais, J. M et al. *Nature* **1998**, 395, 585-588.
- (5) Killian, R. J. of *Geophysical Research* **2004** D23S15 1 of 11